



# Generating power from cellulose in an alkaline fuel cell enhanced by methyl viologen as an electron-transfer catalyst



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## HIGHLIGHTS

- Electricity is directly generated from cellulosic biomass without saccharification process.
- Fuel cell performance is greatly improved by use of methyl viologen as catalyst.
- Maximum power output is 450 mW m<sup>-2</sup> at room temperature and ambient pressure.
- Cellulose is oxidized to short-chain aliphatic carboxylic acids.
- Common reed and red algae show good potential as feedstocks for electricity generation.

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## ABSTRACT

In this work, we developed a single-compartment direct cellulose alkaline fuel cell by using nickel foam as the anode and methyl viologen as an electron transfer catalyst. The maximum power density of the fuel cell at optimal conditions is 450 mW m<sup>-2</sup>. High-performance liquid chromatography detected short-chain aliphatic carboxylic acids in the oxidation products. Using common reed and red algae as fuels, the fuel cell achieved maximum power densities of 295 mW m<sup>-2</sup> and 154 mW m<sup>-2</sup>, respectively.

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## 1. Introduction

To counter the growing threats of the energy crisis and worsening environmental pollution, biomass has been shown as a viable alternative to fossil fuels. Cellulose, which accounts for more than half of the carbon content in plants, has become a popular feedstock for biofuel production. Many researchers have used conventional techniques such as saccharification, fermentation, and energy conversion to convert cellulose into biofuel [1–4], but technical and economic problems hinder these approaches [1,2]. Recently, fuel-cell

technology is quite mature [5–8]; of particular interest are biofuel cells (BFCs), which use enzymes or catalysts to convert energy from biochemical reactions into electrical energy. However, enzyme-based BFCs are usually costly or require complicated processes (e.g., extraction and saccharification) to use; additionally, maintaining the stability of the enzyme used in the BFC and its power output remains difficult [9–12]. These barriers restrict the application of BFCs [13]. Another option is microbial fuel cells (MFCs), which can convert energy in a biodegradable substrate directly into electricity by using microorganisms as a biocatalyst [14–18]. Unfortunately, MFCs do not generate power efficiently. Studies have reported that electricity can be directly generated from cellulose by using noble metal electrodes under alkaline conditions [13]. However, the power density of this process is low, only 44 mW m<sup>-2</sup>, and using noble metals significantly increases the cost of the device.

In this study, we report on generating electricity directly from cellulose by using methyl viologen (MV) as an electron transfer

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catalyst under alkaline conditions. MV has long been used as a redox mediator in MFCs to facilitate electron transfer from microbial cells to the current-collection electrode [19,20]. Recent studies have revealed that using MV as an electron transfer catalyst can significantly improve the performance of direct glucose fuel cells [21,22]. However, the use of MV as an electron transfer catalyst in direct cellulose fuel cells has not been studied before this report. Beyond this topic, in this report we also analyze the final oxidation products of cellulose in the fuel cell and its mechanisms of electricity production.

## 2. Experimental materials and methods

### 2.1. Chemicals and reagents

Methyl viologen (MV) was purchased from J&K Scientific (Beijing, China). Carbon cloth (HCP330), Polytetrafluoroethylene (PTFE) solution (60 wt.%), 10% carbon powder (10% Pt on Vulcan XC-72), and 5% Nafion solution were all purchased from Hesen (Shanghai, China). Carbon black was purchased from Cabot (Tianjin, China). Chemical reference standards for high-performance liquid chromatography (HPLC) were purchased from Sigma–Aldrich. The isopropanol, NaOH, and microcrystalline cellulose used in our experiments were of analytical grade. All solutions were prepared with ultrapure water (Millipore, Milli Q, 18.3 MΩ).

### 2.2. Fuel-cell apparatus and assembly

Our one-chamber fuel cell is made from polymethylmethacrylate (PMMA); a schematic of its structure is shown in Fig. 1. The fuel cell is composed of an anode, an air-breathing carbon-cloth cathode, and a cylindrical internal chamber with a diameter of 30 mm. A Teflon-coated stir bar anchored by a wire was used to circulate the solution contained in the chamber when necessary. The anode substrate was made from Ni foam (purity: 99.9%, pores per inch: 110, density: 380 g m<sup>-2</sup>, average pore size: 590 μm, thickness: 1.7 mm) and purchased from HANBO (Shenzhen, China). A silver/silver chloride electrode was used as the reference electrode. The anode and cathode each had an exposed area of 3.80 cm<sup>2</sup>. All of our experiments were conducted under ambient conditions. A VICTOR 8145B multi-meter (Shanghai, China) was used to monitor the open-circuit voltage (OCV) change of the fuel cell. Cyclic voltammetry (CV) was

conducted using a Corrtest CS120 electrochemical workstation (Wuhan, China).

### 2.3. Dissolution of cellulose

Cellulose (750 mg) was suspended in 20 mL of 2 M NaOH solution, and the mixture was shaken at room temperature (RT). The suspension was stored at −20 °C until it froze. After thawing the sample at RT, we added 20 mL of ultrapure water, producing a 2% (w/v) cellulose solution. The resulting cellulose solution was mixed thoroughly until it became transparent.

### 2.4. Product identification

The chamber of the fuel cell was filled with electrolyte, which contained 1% (w/v) cellulose, 1 M NaOH, and 15 mM MV. A 468-Ω resistor was used as the external resistance between the anodes and cathodes, and the fuel cell was discharged in an incubator at 30 °C. The oxidation products were identified using HPLC after the power generated by the fuel cell decreased significantly. Samples obtained from the fuel cell were centrifuged at 13,000 × g for 5 min. The resulting supernatants were diluted using ultrapure water and filtered through a syringe-tip filter (0.45-μm pore size) (Fisher Scientific) into 2-mL glass vials. The HPLC system (Shimadzu LC-10AVP) was equipped with a UV–Vis detector (Shimadzu SPD-10AVP) and a Rezex RHM-Monosaccharide column (Phenomenex, 300 × 7.8 mm), in which we used 4 mM H<sub>2</sub>SO<sub>4</sub> as the eluent at a flow rate of 0.5 mL min<sup>-1</sup> at 60 °C. The products were identified by comparing their retention times to those of corresponding standards.

### 2.5. Performance of the fuel cell, using common reed and red algae as fuels

Common reed (*Phragmites* sp.) was collected from the shores of Qingnian Lake (Tianjin, China), and red algae (*Gracilaria* sp.) was collected from the coastal waters of Qingdao (Shandong, China). They were washed and air-dried to produce samples of 90% dry matter, after which they were chopped and milled using a CX350A grinder (Shenghi, Shanghai, China). The resulting powder was passed through an 80-mesh sieve and dissolved as described above. The electrical output of the fuel cell was monitored by measuring the potential difference (voltage) between the anode and the cathode across the external resistance with an MPS-010602 data acquisition unit (Morpheus, Beijing, China). The specific capacity (SC) of the feedstock is calculated using equation (1).

$$SC = (N \times C)/W \quad (1)$$

where  $N$  is the conversion constant (0.27778 mAh Cullen<sup>-1</sup>),  $C$  is the total recovered coulombs (obtained by integrating the current over time), and  $W$  is the weight of the cellulosic biomass.

## 3. Results

### 3.1. Effect of nitrogen sparging on fuel-cell performance

To test how anaerobic conditions affected power generation, we sparged the fuel cell chamber with oxygen-free nitrogen. The results of this experiment, shown in Fig. 2a, indicate that nitrogen sparging improves cell performance. The polarization curve indicates that nitrogen sparging increases the maximum current density from 307 to 456 mA m<sup>-2</sup>; additionally, sparging increased the peak power density from 2.02 to 2.65 mW m<sup>-2</sup>. Thus, we performed all further experiments under anaerobic conditions.

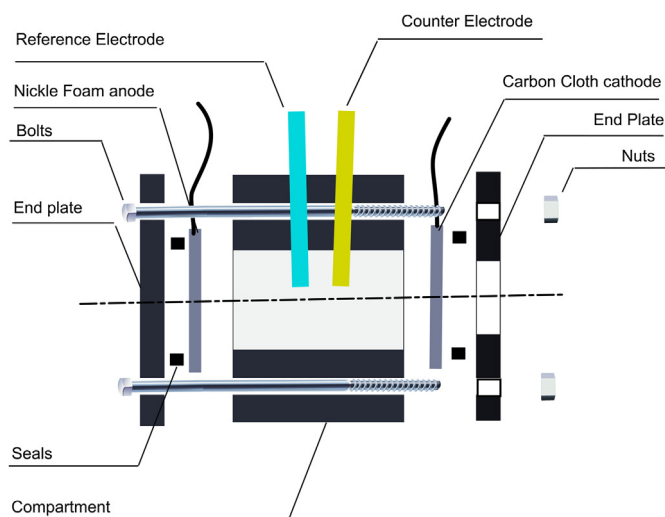
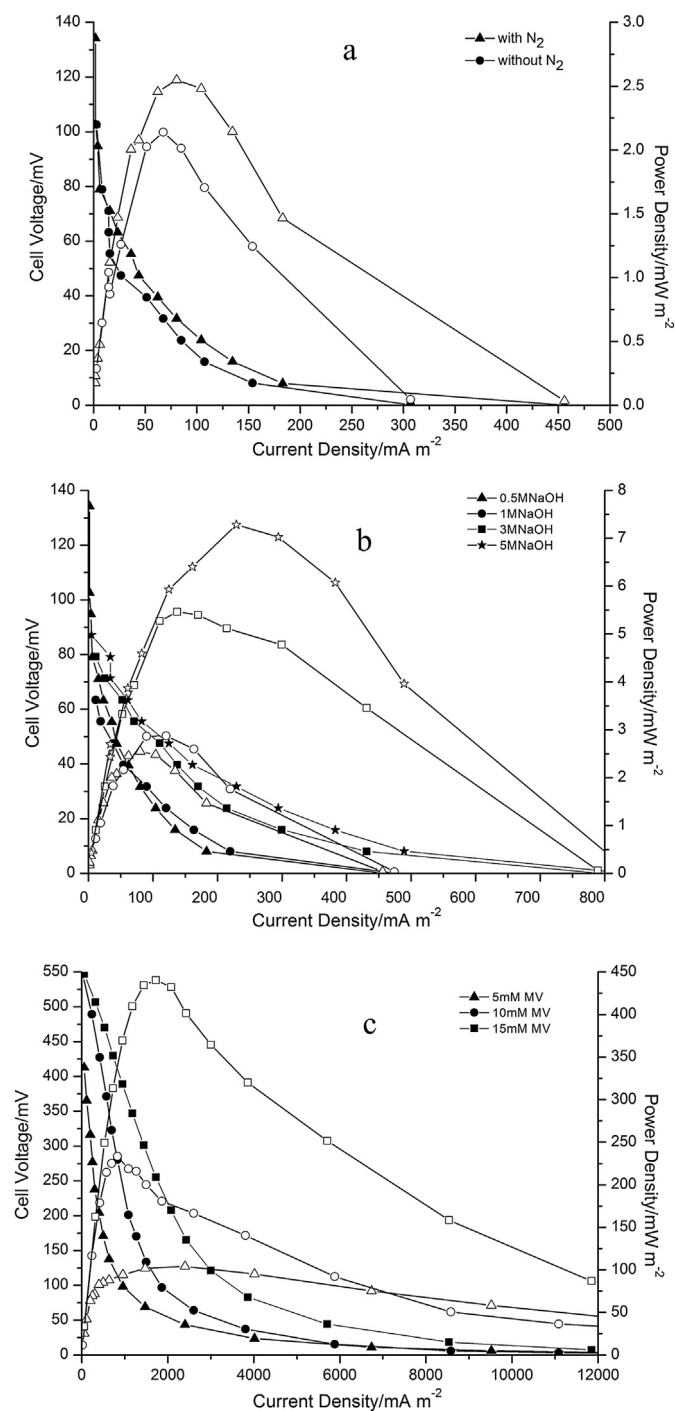


Fig. 1. Schematic of the structure of a direct cellulose alkaline fuel cell.



**Fig. 2.** Influence of nitrogen sparging (a), NaOH concentration (b), and MV concentration (c) on the performance of the alkaline fuel cell.

### 3.2. Effect of NaOH concentration on fuel-cell performance

Fig. 2b shows, at a 1% (w/v) cellulose concentration, that cell performance improved with KOH concentration in the range we tested. Specifically, increasing the KOH concentration from 0.5 to 5 M increased the peak power density from 2 to 7.5 mW m<sup>-2</sup>.

### 3.3. Effect of MV concentration on fuel-cell performance

Fig. 2c shows, at 5.0 M NaOH and 1% (w/v) cellulose, that increasing the MV concentration improved the fuel cell

performance by increasing the electron transfer efficiency. Specifically, increasing the MV concentration from 0 mM to 15 mM increased the open-circuit voltage from 0.135 V to 0.57 V and the peak power density from 7.5 to 450 mW m<sup>-2</sup>, a 60-fold increase.

### 3.4. Electrocatalytic properties of MV for cellulose oxidation in alkaline conditions

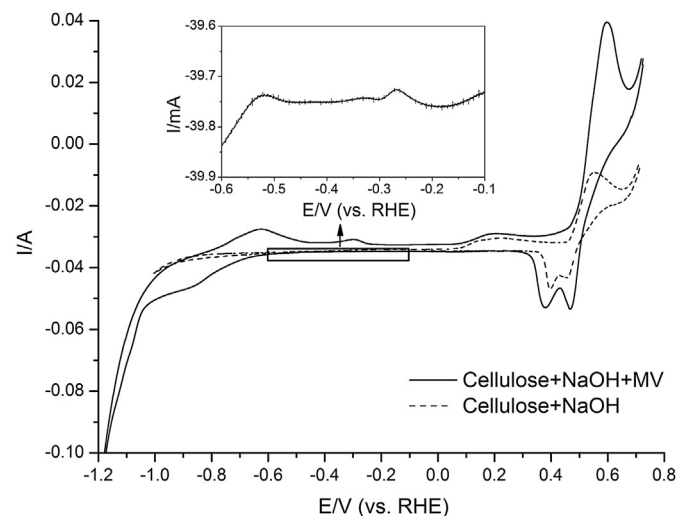
To study the anodic oxidation of cellulose in alkaline condition, we used cyclic voltammetry (CV) in the range of potential between -1.2 and 0.8 V vs. RHE (reversible hydrogen electrode). In 5 M NaOH, the cellulose oxidation peaks appear at -0.52 V, -0.25 V, 0.2 V, and 0.55 V (Fig. 3). Adding MV into the solution causes two new oxidation peaks to appear at -0.6 and -0.3 V, which correspond to the oxidation peaks of MV<sup>0</sup> and MV<sup>•+</sup>. Additionally, adding MV to the fuel cell dramatically increases the anodic peak current.

### 3.5. Product identification from cellulose oxidation

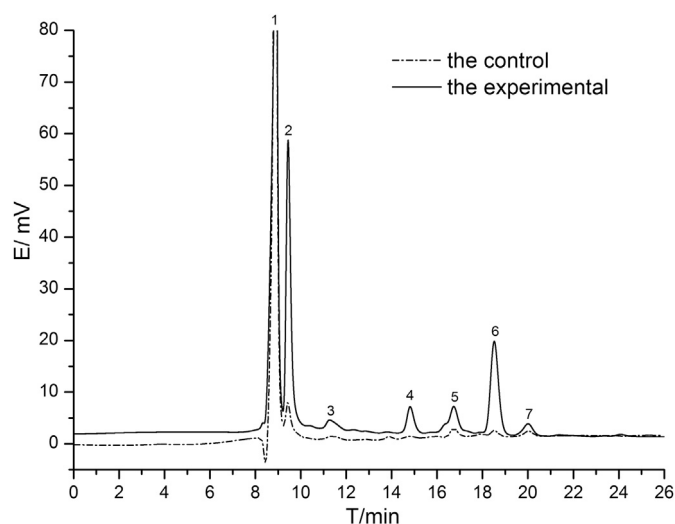
Fig. 4 shows a chromatogram of the oxidation products, which reveals the presence of oxalic acid (peak 2), glucuronic acid or glucaric acid (peak 3), glyceric acid (peak 4), glycolic acid (peak 5), formic acid (peak 6), and acetic acid (peak 7). These results suggest that cellulose oxidized into short-chain aliphatic carboxylic acid in our experiment.

### 3.6. Evaluating common reed and red algae as fuels for direct electricity generation

The polarization and power density curves of a fuel cell at 5 M NaOH and 15 mM MV using common reed or red algae as fuel are shown in Fig. 5a and b, respectively. Using common reed as fuel produced an open-circuit voltage, limiting current density, and maximum power density of 395 mV, 1952 mA m<sup>-2</sup>, and 294 mW m<sup>-2</sup>, respectively. For red algae as fuel, those three parameters were 417 mV, 520 mA m<sup>-2</sup>, and 154 mW m<sup>-2</sup>, respectively. As Fig. 6 indicates, the specific capacities of microcrystalline cellulose, common reed, and red algae are 41.2092, 40.0606 and 24.4260 mAh g<sup>-1</sup>, respectively. Thus, all these feedstocks show potential for directly generating electricity in our fuel cell.



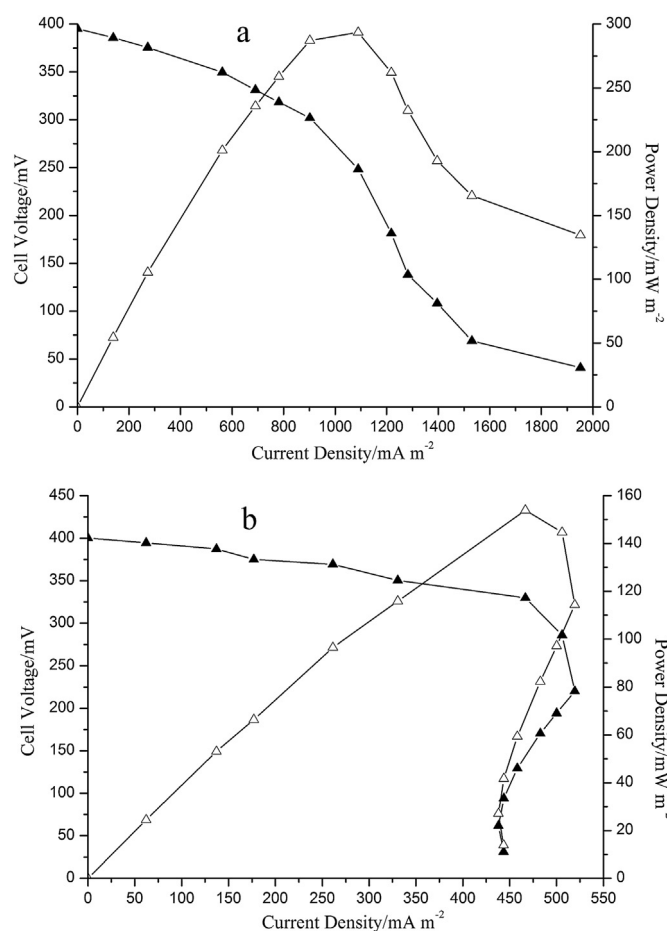
**Fig. 3.** CV measurement of Ni foam in a fuel cell with 1% cellulose, 5 M NaOH, and 15 mM MV at a scan rate of 5 mV s<sup>-1</sup>. Inset: enlarged scale graph in the cellulose oxidation region between -0.6 V and -0.1 V.



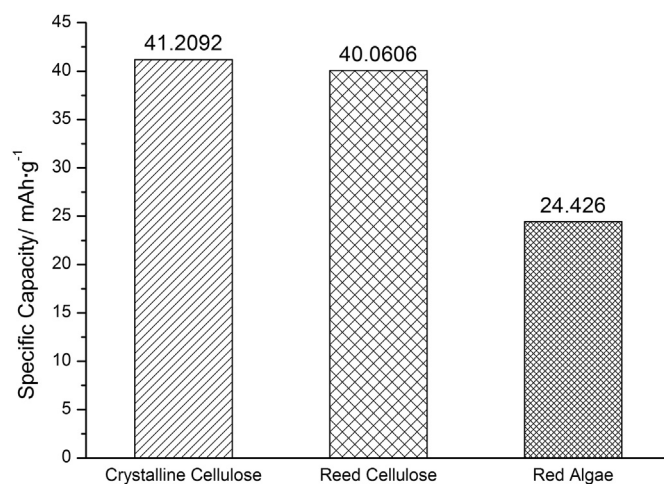
**Fig. 4.** Liquid chromatography of cellulose oxidation products. Peak 1: solvent; peak 2: oxalic acid; peak 3: glucuronic acid or glucaric acid; peak 4: glyceric acid; peak 5: glycolic acid; peak 6: formic acid; peak 7: acetic acid.

#### 4. Discussion

Releasing the energy stored in carbohydrate biomass as clean electric power requires efficient, economical catalysts. Our previous



**Fig. 5.** Polarization curves and power profiles for fuel cells fed with common reed (a) or red algae (b) in a solution with 5 M NaOH and 15 mM MV.

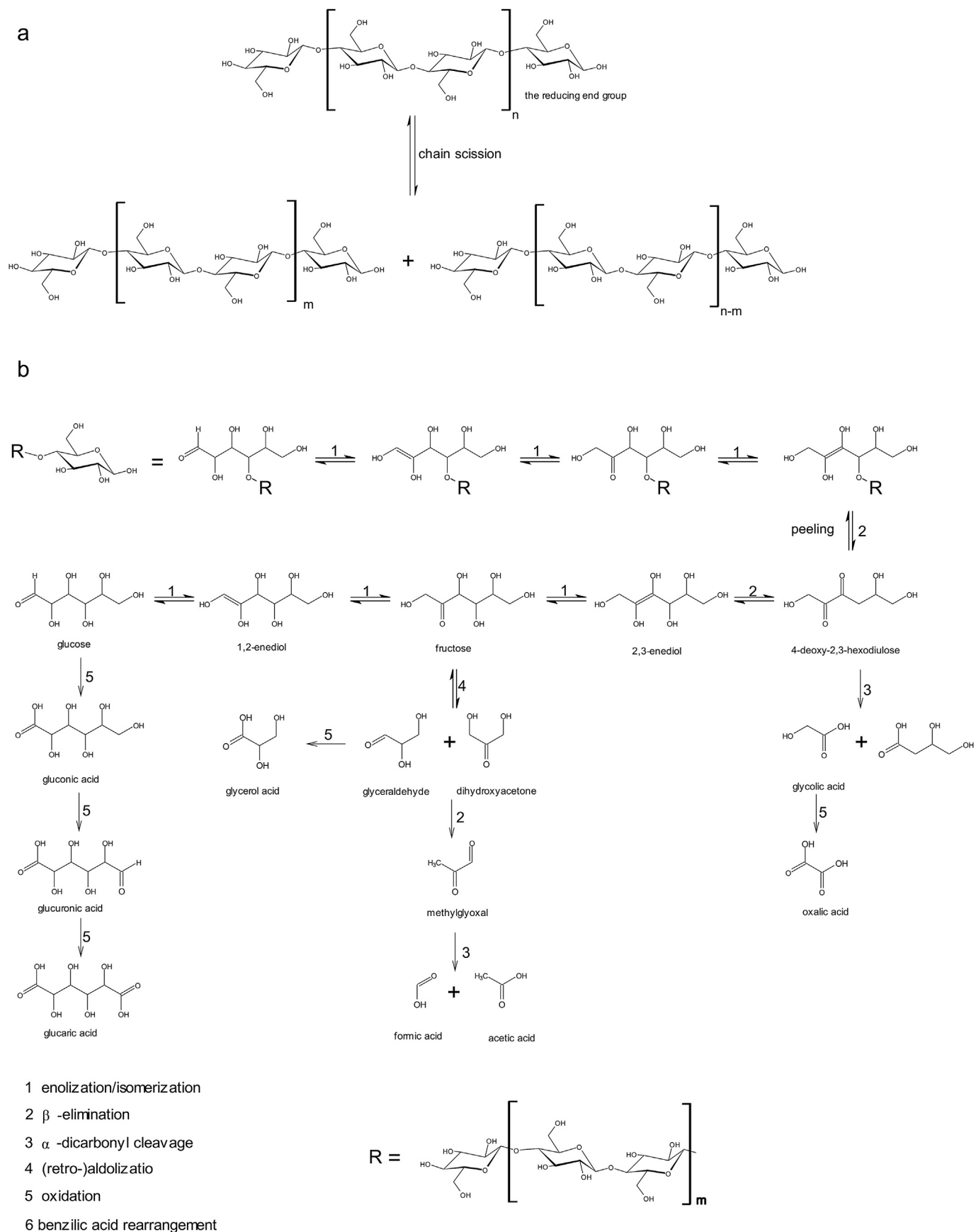


**Fig. 6.** Specific capacity of microcrystalline cellulose, common reed, and red algae measured at an external resistance of 468  $\Omega$ .

study showed that adding MV dramatically improved the performance of a direct glucose fuel cell [22], whereas the present work further demonstrates that cellulosic biomass can be converted to electricity via the same catalyst, a new and promising way to couple cellulosic biomass disposal with energy recovery. Our biomass-fed fuel cell produced a maximum power of  $450 \text{ mW m}^{-2}$ , which is more than 10 fold higher than that reported by Sugano et al. ( $44 \text{ mW m}^{-2}$ ) [13]. Additionally, they used gold and platinum as their anode and cathode, respectively, increasing the cost of their device.

Cellulose is the most abundant organic material on Earth. It is a linear macromolecule composed of up to 10,000 (1,4)- $\beta$ -D-glucopyranose units. The cellulose molecule is terminated in a non-reducing end and a reducing one. The reducing end is a latent aldehyde and, like an aldehyde functional group, responds to both reduction and oxidation. Reports have identified three distinct reaction pathways that contribute to alkaline degradation of cellulose: peeling, stopping, and mid-chain scission [23]. Mid-chain scission can generate new reducing end groups, while peeling occurs at the reducing end group and involves converting the terminal anhydroglucose unit into small molecules [24]. Our HPLC results allow us to establish the proposed reaction pathways for the conversion of cellulose into short-chain aliphatic carboxylic acids, shown in Fig. 7a and b. We propose that the cellulose oxidation in our fuel cell involves the following reactions: mid-chain scission, peeling, enolization/isomerization,  $\beta$ -OH elimination,  $\alpha$ -dicarbonyl cleavage and (retro-)aldolization.

The results of our CV measurements of the cellulose samples show an oxidation peak at  $-0.52 \text{ V}$ , which we consider the first step of cellulose oxidation on the Ni anode. Also involved should be chemisorption and dehydrogenation of the hemiacetalic carbon 1 atom (C1) of the reducing end, similar to glucose oxidation [25]. An oxidation peak at  $0.2 \text{ V}$  appears regardless of the presence of the MV, indicating it also corresponds to cellulose oxidation on the Ni anode. This peak can be assigned to the oxidation of the chemisorbed cellulose, catalyzed by the adsorbed hydroxide. The last oxidation peak located at  $0.55 \text{ V}$  can be assigned to the Ni(II)/Ni(III) redox couple [25]. Nickel can catalyze glucose oxidation in an alkaline solution, mainly driven by the Ni(II)/Ni(III) redox couple [26]. Therefore, at high potentials the reducing end groups of cellulose are likely to be oxidized along with the oxidation of Ni(II) to Ni(III). However, forming Ni(III) is difficult in the range of anode potentials found in our alkaline fuel cell ( $-0.45$  to  $0.1 \text{ V}$  vs. RHE). Therefore, cellulose oxidation during this step might be negligible.



**Fig. 7.** Mid-chain scission of cellulose under alkaline conditions (a) and proposed pathways of cellulose oxidation in the alkaline fuel cell (b).



Viologens exhibit a fast, reversible electrochemical response at negative potentials, which makes them useful redox mediators for many enzymatic reactions [27]. MV has been used as a redox mediator in microbial fuel cells to facilitate electron transfer from microbial cells to the electrode [19,20]. In solution, the reduction reaction of MV is as follows:



MV dissolved in a deaerated solution can be reduced by cellulose under relatively high concentrations of NaOH.  $\text{MV}^{2+}$  is colourless, while  $\text{MV}^{\bullet+}$  is blue. Mixing MV into water leaves the solution colourless, but mixing cellulose, NaOH, and MV together immediately turns the solution blue, indicating that the  $\text{MV}^{2+}$  has been reduced to  $\text{MV}^{\bullet+}$ . The redox couple  $\text{MV}^{2+}/\text{MV}^{\bullet+}$  has a low potential, making it suitable as an electron-transfer mediator on the Ni anode. The potential of the cellulose moiety decreases with increased pH, but the potential of MV does not [28]; therefore, MV would receive the electron from the cellulose moiety more easily in the higher pH solution. Our results indicate that MV plays an important role in improving fuel-cell performance. Adding MV to the chamber caused two new oxidation peaks appeared at  $-0.6$  V and  $-0.3$  V, which we attributed to the oxidation of methyl viologen ( $\text{MV}^0$  and  $\text{MV}^{\bullet+}$ ) on the anode surface. Adding MV also greatly enhances the current produced by the redox reaction of Ni, indicating an interaction between methyl viologen and the surface of the Ni electrode. Furthermore, the redox couple  $\text{MV}^{2+}/\text{MV}^{\bullet+}$  has a low redox potential, and the small size of those species benefits mass transfer; thus, this couple offers an easy way to transfer electrons between the cellulose and Ni electrode surface. Consequently, adding MV dramatically increased the anodic peak current. MV-catalyzed cellulose oxidation is likely similar to that of glucose: the cellulose molecules first release electrons, which are then captured by the  $\text{MV}^{2+}$ , which reduces to  $\text{MV}^{\bullet+}$ .  $\text{MV}^{\bullet+}$  then oxidizes back to  $\text{MV}^{2+}$  and transfers the electron to the Ni anode [22]. When the electron reaches the anode, it immediately moves through the external circuit to the cathode. Oxygen at the cathode captures the electron and is reduced to  $\text{OH}^-$ , completing the reaction. Considering the entire process, MV acts as the electron-transfer catalyst without being consumed. The presence of MV greatly accelerates the oxidation of cellulose and improves the performance of the fuel cell.

The performance of the fuel cell is affected by many factors besides MV concentration, including nitrogen sparging. Without sparging, both the anode and oxygen can serve as the terminal electron acceptor, and any  $\text{O}_2$  in the solution can compete with the anode to accept electrons [29]. Nitrogen sparging removes  $\text{O}_2$  from the solution and allows electron transport to the MV and, finally, to the anode. Thus, anaerobic condition in the chamber benefits cell performance. The slope of the polarization curve in Fig. 2b decreases with increasing NaOH concentration, indicating that increasing the NaOH concentration can reduce the resistance of the cell. Increasing NaOH concentration not only increases the electrolyte conductivity, but also supplies more  $\text{OH}^-$  ions, which are needed for oxidation to occur in the solution. Thus, increasing the NaOH concentration enhances the kinetics of cellulose oxidation, which lowers the anode activation loss and compensates for the increased Ohmic loss, improving the cell performance overall [7].

We observed an overshoot phenomenon while analyzing the power curves of fuel cell fed with red algae. In the overshoot region, the current decreases as the potential decreases. This phenomenon can be attributed to a decrease of the anode electroactivity in the high-potential region, caused by lack of sufficient electron-transfer components to shuttle electrons at the rate needed for the more positive potentials in this case [30]. This overshoot phenomenon is

**Table 1**

Electricity production using cellulosic biomass as fuel.

Energy sources	Energy conversion technology	Open circuit potential (V)	Maximum power density ( $\text{mW m}^{-2}$ )	Ref.
Cellulose	Microbial fuel cell	0.8	59	[33]
Cellulose	Microbial fuel cell	ca. 0.5	ca. 80	[34]
Cellulose	Microbial fuel cell	ca. 0.8	ca. 100	[35]
Cellulose	Alkaline Fuel cell	ca. 0.44	44	[13]
Cellulose	Alkaline fuel cell	0.57	450	This study
Common reed	Alkaline fuel cell	0.395	295	This study
Red algae	Alkaline fuel cell	0.417	154	This study

not limited to MFC research; it has also been reported for conventional fuel cells such as direct methanol fuel cells [31] and proton exchange membrane (PEM) fuel cells [32]. In our experiments the overshoot pattern only appears in the fuel cell fed with red algae. Red algae contain high amounts of agar, which can form a gel-like substance when dissolved in a NaOH solution. The solution with red algae in our experiment was very viscous and sticky, which greatly hindered mass transfer and led to power overshoot.

Common reed and red algae are ideal feedstocks for energy production and abundant in temperate and tropical regions. Using cellulosic biomass as fuel in our fuel cell improves its performance to levels greater than those previously reported, as summarized in Table 1. Our results demonstrate that, by using MV as the catalyst and Ni foam as the anode, cellulosic biomass can be directly converted into electricity, providing a new avenue for using out most abundant cellulosic resources.

## 5. Conclusions

In this report we developed and tested a cellulose-air alkaline fuel cell that does not use noble metal catalysts, is simple to use, and can be fed with a variety of inexpensive, abundant materials. Adding methyl viologen to our fuel cell greatly improved its performance, which also depended on the concentrations of MV and NaOH in the electrolyte solution. The maximum power output of our cell was  $450 \text{ mW m}^{-2}$ , higher than those of most existing cellulose-fed fuel cells, such as enzymatic fuel cells and MFCs. Our HPLC results indicated that cellulose can be oxidized into short-chain aliphatic carboxylic acids, such as oxalic acid, glucuronic acid or glucaric acid, glyceric acid, glycolic acid, formic acid, and acetic acid. Finally, we evaluated common reed and red algae as fuels and demonstrated their potential direct generation of electricity.

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## References

- [1] R.C. Saxena, D.K. Adhikari, H.B. Goyal, *Renew. Sustain. Energy Rev.* 13 (2009) 167–178.
- [2] E.M. Rubin, *Nature* 454 (2008) 841–845.
- [3] S.K. Chaudhuri, D.R. Lovley, *Nat. Biotechnol.* 21 (2003) 1229–1232.
- [4] I. Willner, *Science* 298 (2002) 2407–2408.
- [5] T. Yang, L.Y. Meng, N. Huang, *J. Power Sources* 224 (2013) 132–138.
- [6] E.M. Sommer, L.S. Martins, J.V.C. Vargas, J.E.F.C. Gardolinski, J.C. Ordóñez, C.E.B. Marino, *J. Power Sources* 213 (2012) 16–30.
- [7] L. An, T.S. Zhao, S.Y. Shen, Q.X. Wu, R. Chen, *J. Power Sources* 196 (2011) 186–190.
- [8] M. Fatih Demirbas, *Appl. Energy* 88 (2011) 3473–3480.

- [9] J. Kim, H. Jia, P. Wang, *Biotechnol. Adv.* 24 (2006) 296–308.
- [10] S.C. Barton, J. Gallaway, P. Atanassov, *Chem. Rev.* 104 (2004) 4867–4886.
- [11] S. Kerzenmacher, J. Ducrée, R. Zengerle, F. von Stetten, *J. Power Sources* 182 (2008) 1–17.
- [12] H.A. Sedky Hassan, Y.S. Kim, S.E. Oh, *Enzyme Microb. Technol.* 51 (2012) 269–273.
- [13] Y. Sugano, M. Vestergaard, H. Yoshikawa, M. Saito, E. Tamiya, *Electroanalysis* 22 (2010) 1688–1694.
- [14] D.R. Bond, D.R. Lovley, *Appl. Environ. Microbiol.* 69 (2003) 1548–1555.
- [15] J.R. Kim, S.H. Jung, J.M. Regan, B.E. Logan, *Bioresour. Technol.* 98 (2007) 2568–2577.
- [16] H.J. Kim, H.S. Park, M.S. Hyun, I.S. Chang, M. Kim, B.H. Kim, *Enzyme Microb. Technol.* 30 (2002) 145–152.
- [17] B.E. Logan, C. Murano, K. Scott, N.D. Gray, *Water Res.* 39 (2005) 942–952.
- [18] B.E. Logan, J.M. Regan, *Environ. Sci. Technol.* 40 (2006) 5172–5180.
- [19] A.C. Greene, B.K.C. Patel, A.J. Sheehy, *Int. J. Syst. Evol. Microbiol.* 47 (1997) 505–509.
- [20] G.D. Hitchens, *Trends Biochem. Sci.* 14 (1989) 152–155.
- [21] G.D. Watt, D. Hansen, D. Dodson, M. Andrus, D. Wheeler, *Renew. Energy* 36 (2011) 1523–1528.
- [22] X.H. Liu, M.Q. Hao, M.N. Feng, L. Zhang, Y. Zhao, X.W. Du, G.Y. Wang, *Appl. Energy* 106 (2013) 176–183.
- [23] C.J. Knill, J.F. Kennedy, *Carbohydr. Polym.* 51 (2003) 281–300.
- [24] M.A. Glaus, L.R. Van Loon, *Environ. Sci. Technol.* 42 (2008) 2906–2911.
- [25] M. Jafarian, F. Forouzandeh, I. Danaee, F. Gopal, M.G. Mahjani, *J. Solid State Electron.* 13 (2009) 1171–1179.
- [26] J.P. Li, J.G. Yu, Q.Y. Lin, *Anal. Lett.* 43 (2010) 631–643.
- [27] E. Casero, A. Martinez, G. de Quesada, J. Jin, M.C. Quintana, F. Pariente, H.D. Abruña, L. Vázquez, E. Lorenzo, *Anal. Chem.* 2 (2006) 530–537.
- [28] C.L. Bird, A.T. Kuhn, *Chem. Soc. Rev.* 10 (1981) 49–82.
- [29] E. Katz, A.N. Shipway, I. Willner, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), *Handbook of Fuel Cells*, 2003, pp. 355–381. Chichester.
- [30] X. Zhu, J.C. Tokash, Y. Hong, B.E. Logan, *Bioelectrochemistry* 90 (2013) 30–35.
- [31] J. Ge, H. Liu, *J. Power Sources* 142 (2005) 56–69.
- [32] A.A. Kulikovskiy, A. Kucernak, A.A. Kornyshev, *Electrochim. Acta* 50 (2005) 1323–1333.
- [33] Z. Ren, T.E. Ward, J.M. Regan, *Environ. Sci. Technol.* 41 (2007) 4781–4786.
- [34] F. Rezaei, T.L. Richard, R. Brennan, B.E. Logan, *Environ. Sci. Technol.* 41 (2007) 4053–4058.
- [35] F. Rezaei, T.L. Richard, B.E. Logan, *Biotechnol. Bioeng.* 101 (2008) 1163–1169.